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TI - Hydroxyl gp. terminated telechelic polymers prodn. - by polymerising monomers with halogen cpds. in presence of initiators and converting halogen end gps. to hydroxy
IW - HYDROXYL GROUP TERMINATE TELECHELIC POLYMER PRODUCE POLYMERISE MONOMER HALOGEN COMPOUND PRESENCE INITIATE CONVERT HALOGEN END GROUP HYDROXY
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AB - J04132706 OH gp.-end telechelic polymers are produced by polymerising (a) monomers in amts. of 0.01-10 times mole to (b) halogen cpds. of formula R1X1X2 (I) in the presence of (b) and (c) polymerisation initiators, and converting the end gp. of (d) halogen-end telechelic polymers to OH by replacement.
- (R1 = a 1-8C dihydric hydrocarbon gp; X1, X2 = Br or I).
- Pref. replacement is hydrolysis in the presence of (e) basic catalysts, pref. cpds. contg. alkali metals. Replacement is performed between (d) and diol cpds. of formula HOR2OH (II) and/or HO-(R2-O)n-H (III) in the presence of (e). (R2 = opt. substd. 1 - 18 C dihydric hydrocarbon gp; n = an integer of 1-1000.
- USE/ADVANTAGE - The telechelic polymers are useful for the mfr. of resins, paint, adhesive and sealant and as precursors for telechelic polymers for crosslinking age (Dwg. 0/0)

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(54) Title of the invention: Process to produce a telecheric polymer having a hydroxyl group at the ends

(21) Patent Application No. 2-255508

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[TN: A word with an asterisk can be read differently due to nature of Japanese.]

SPECIFICATION

1. Title of the invention:

A process to produce a telecheric polymer having a hydroxyl group at the ends

2. Claims:

1) A process to produce a telecheric polymer having a hydroxyl group at the ends characterized by: in the presence of a halogen compound, represented by [the following] Chemical Formula (I) and a polymerization initiator (b), polymerizing a polymeric monomer (c), which is 0.01~10 times mole in relation to the above described halogen compound, to obtain a telecheric polymer having a halogen at the

ends; and thereafter by converting,utilizing a substitution reaction, the end group of the telecheric polymer having a halogen at the ends into a hydroxyl group;

$R^1X^1X^2$ (I)

(in the formula, R^1 is a bivalent hydrocarbon group of C1~C[TN: illegible] and X^1 and X^2 are independent and are either bromine or iodine.)

2) A process described in Claim (1) in which the substitution reaction is hydrolysis in the presence of a basic catalyst (d).

3) A process described in Claim (2) in which the basic catalyst (d) is a compound containing an alkali metal.

4) A process described in Claim (1) in which the substitution reaction is [TN: sic. presumably "a reaction between" is missing. Compare this with Claims 6 and 8, all of which contain "a reaction between"], in the presence of a basic catalyst (e), the telecheric polymer having a halogen at the ends, a diol compound (f), represented by Formula (II) and/or Formula (III).

HOR^2OH (II)

(in the formula, R^2 is a bivalent hydrocarbon group of C1 ~ C[TN: illegible] which may contain a substituent.)

$HO-(R^2-O)_n-H$ (III)

(in the formula, R^2 is a bivalent hydrocarbon group of C1 ~ C[TN: illegible] which may contain a substituent and n is a whole number of 1 ~ 1000.)

5) A process described in Claim (4) in which the basic catalyst (e) is a compound containing alkali metal.

6) A process described in Claim (1) in which the substitution reaction is a reaction between the telecheric polymer having a halogen at the ends and an amine compound (g) containing a hydroxyl group, represented by Formula (IV).

R^4NHR^5OH (IV)

(in the formula, R^4 is hydrogen or alkyl group of $C_1 \sim C$[TN: illegible] and R^5 is a bivalent hydrocarbon group of $C_1 \sim C$[TN: illegible].)

7) A process described in Claim (6) in which the the amine compound (g) containing a hydroxyl group is a secondary amine compound.

8) A process described in Claim (1) in which the substitution reaction is a reaction between the telecheric polymer having a halogen at the ends and a carboxylate compound (h) containing a hydroxyl group, represented by Formula (V).

$$HOR^6COOM \qquad (V)$$

(in the formula, R^6 is a bivalent hydrocarbon group of $C_1 \sim C$[TN: illegible] and M is an alkali metal.)

9) A process described in Claim (1) in which the polymeric monomer (c) contains an acrylic ester and/or a methacrylic ester.

10) A process described in Claim (1) in which the halogen compound (a) is an iodine compound.

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention relates to a process to produce a telecheric polymer having a hydroxyl group at the ends which itself, as a polymer having a reactive group at the ends, is very useful as a raw material for polyurethane resin, polyester resin, coating materials, adhesives, sealing materials, etc. , and which can be easily convertible to a vinyl type cross-linking agent having a functional group at the ends such as a vinyl group, a (meth)acryloyl group, etc.

(Prior Art and the Problems that the Invention is to Solve)

A telecheric polymer ideally has one functional group at each of both ends. Because of that, when it is used as a raw material for various resins such as polyurethane resin and epoxy resin, it has a significant advantage that the characteristics of the telecheric

polymer itself are thoroughly exhibited since there is no non-reactant which compromises the physical properties of the material and is absorbed in the resin structure and the distance between the reaction points (between the cross-linking points) becomes constant and produces a uniform structure. Because of this, it is very useful as a raw material for various resins, coating materials, adhesives, sealing materials, etc. Among all, the telecheric polymer having a hydroxyl group at the ends is very useful industrially as a raw material for polyurethane resin, polyester resin, etc. Currently, telecheric polymers used industrially are generally polyether type, polyester type, etc., but they have drawbacks of poor weatherability and a water resistant property. A vinyl type telecheric polymer has a problem of not easily being synthesized industrially. A polybutadiene telecheric polymer is also known, but this does not sufficiently solve the deficiencies of the polyether type and the polyester type telecheric polymers. Especially the drawbacks of the polyether and polyester type telecheric polymers are presumably solved by acrylic telecheric polymers. However, a process to produce industrially a telecheric polymer using a polar polymeric monomer such as acrylic esters and methacrylic esters currently is not established.

Halogen atoms such as chlorine, bromine, iodine, etc. are active reactive functional groups. Using a telecheric polymer having such halogen atoms at both ends as an intermediate, by utilizing a hydrolysis of halogen atoms at the ends and a substitution reaction of a diol compound, or an amine compound, a carboxylate compound, etc. having a hydroxyl group at the ends, it is possible to easily synthesize a telecheric polymer having a hydroxyl group at the ends.

As a technique to produce a vinyl type polymer having halogen atoms at both ends of the polymer, conventionally there has been used telomerization in which carbon tetrachloride, etc. is used as a chain transfer agent.

Such representative example is a polymerization of ethylene using carbon tetrachloride. The polymer obtained from such reaction has a structure [described below],

$$Cl - (CH_2 - CH_2)_n - CCl_3 \quad (\text{where } n=1\sim10)$$

and has halogen atoms at both ends, but the number of halogen atoms at the ends is

irregular such as 1 through 3. Even if a hydrolysis reaction or a substitution reaction of diol compounds, or amine compounds and carboxylate compounds having a hydroxyl group is performed, the structure after a reaction becomes irregular because of a reaction of only one atom among three halogen atoms at one end, a reaction of two atoms or a reaction of three atoms, resulting in an inability to synthesize an ideal telecheric polymer.

The objective of the present invention is to provide a process to produce easily and inexpensively a telecheric polymer having a hydroxyl group at the ends which itself, as a polymer having a reactive group at the ends, is very useful as a raw material for polyurethane resin, polyester resin, coating materials, adhesives, sealing materials, etc., and to produce easily and inexpensively a telecheric polymer having a hydroxyl group at the ends, for which the synthesis is complicated and difficult, by using a telecheric polymer having a halogen at the ends, obtained from the synthesis of a telomerization reaction, as an intermediate and by converting the halogen atoms at the ends to hydroxyl groups using the substitution reaction.

(Means to Solve the Problems and the Operation)

The inventors discovered and thus reached the invention that, in the presence of a compound containing, in one molecule, two halogen atoms comprised of bromine and/or iodine, and a polymerization initiator, by performing hydrolysis of highly reactive halogen atoms at the ends of the telecheric polymer having halogen at the ends, which is obtained from a method to polymerize polymeric monomers, or a substitution reaction of a diol compound, or an amine compound, a carboxylate compound, etc. having a hydroxyl group, a telecheric polymer having the hydroxyl group at the ends can be easily and inexpensively synthesized even in the case where the polymeric monomers are polar monomers including acrylic esters and methacrylic esters.

Specifically, the present invention relates to a process to produce a telecheric polymer having the hydroxyl group at the ends characterized by: in the presence of a halogen compound (a) represented by Formula (I) [below] and a polymerization initiator (b),

$$R^1X^1X^2 \qquad (I)$$

(in the formula, R^1 is a bivalent hydrocarbon of C1~C[TN: illegible, could be "3"] and X^1 and X^2 are independent and are either bromine or iodine), polymerizing a polymeric monomer (c), which is 0.01~10 times mole per the halogen compound (a), so as to produce a telecheric polymer having halogen at the ends; and utilizing the substitution reaction, followed by converting the telecheric polymer having halogen at the ends into the hydroxyl group.

Examples of the halogen compounds (a) represented by Formula (I) used in the invention are dibromomethane, 1,1,-dibromoethane, 1,2-dibromoethane, 1,2-dibromopropane, 1,3-dibromopropane, 1,3-dibromobutane,1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromehexane, 1,7-dibromoheptane, 1,8-dibromooctane, 1,2-dibromoethylene, 2,3-dibromopropane, diiodomethane, 1,1-diiodoethane, 1,2-diiodoethane, 1,2-diiodoethylene, bromoiodomethane, 1-bromo-2-iodoethane, etc. One kind of these or a mixture of two or more kinds of these can be used.

Of these, iodine compounds such as diiodomethane, 1,1-diiodoethane, 1,2-diiodo-ethane, 1,2-diiodoethylene, etc. are very preferable because they have a large chain transfer constant, good telomerization efficiency and the number of the halogen functional groups ((Fn(X)) at the ends of the telecheric polymer formed becomes greater (approaching 2.0).

Examples of the polymeric monomers (c) used in the invention are: acrylic esters such as acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, stearyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, glycidyl acrylate, 2-N,N-dimethylaminoethyl acrylate, and its tetraacrylate, monoacrylic ester of polyethylene oxide; methacrylic esters such as methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, stearyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate, glycidyl methacrylate, 2-N,N-dimethylaminoethyl methacrylate and its tetramethacrylate, monomethacrylic ester of polyethylene oxide, etc.; maleic acid, maleic anhydride, monoalkyl ester and dialkyl ester of maleic acid; phthalic acid, monoalkyl ester and

dialkyl ester of phthalic acid; styrene derivatives of styrene, α-methylstyrene, chloromethylstyrene, styrene sulfonic acid [TN: literal translation]; maleimide derivatives of maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide, cyclohexylmaleimide; polymeric monomers containing a nitrile group such as acrylonitrile, methacrylonitrile, etc.; polymeric monomers containing an amide group such as acrylamide, methacrylamide, etc.; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate, etc.; dienes such as butadiene, isoprene, etc.; vinyl chloride, vinylidene chloride, allyl chloride, allyl alcohol, etc. One kind of these or a mixture of two or more kinds of these can be used.

Of these, the use of acrylic esters and methacrylic esters produces a telecheric polymer having good weatherability and water resistance which cannot be obtained in polyether and polyester type telecheric polymers, so it is preferable to use acrylic esters and/or methacrylic esters as an essential component and the preferable ratio is 50~100% by weight in the polymeric monomers (c).

The polymeric monomer (c) must be 0.01~10 times mole in relation to the halogen compound (a). When the amount used is less than 0.01 times mole, the progress of polymerization is inhibited, causing a decrease in the conversion. When the amount of use exceeds 10 times mole, sufficient chain transfer is not caused and the number of the halogen functional groups at the ends of the formed polymer decreases. A preferable range is 0.1~5 times mole.

Any polymerization initiators (b) which are conventionally used for a radical polymerization of polymeric monomers can be used without limitation. The amount of use can be in a wide range according to the characteristics of the telecheric polymer to be obtained, but it is preferable to use in an amount such that the mole ratio between the halogen compound (a) and the polymerization initiator (b) is 50~500. When the mole ratio is less than 50, the chain transfer to the halogen compound (a) becomes insufficient, which may result in a decrease of the number of halogen functional groups at the ends of the polymer obtained. When it exceeds 500, the progress of polymerization is inhibited, which may cause a decrease in the conversion.

In the polymerization [process], depending upon need, a solvent can be freely used, in addition to the halogen compound (a), the polymeric monomer (c) and the polymerization initiator (b). However, it is not preferable to use a large quantity of a solvent having a large chain transfer constant, e.g., a chain transfer constant of 1×10^{-4}, because the number of halogen functional groups at the ends of the obtained polymer decreases. Polymerization temperature can be freely selected, but a preferable temperature is 20~120°C and more preferable is 20~80°C. Especially 20~50°C is preferable because even if bimolecular termination occurs, the halogen atoms can be efficiently introduced to both ends of the polymer by avoiding the formation of double bonding caused by the disproportionation termination and without decreasing the number of the halogen functional groups at the ends caused by the rebonding termination.

Specific examples of the polymerization initiators (b) are: azo type initiators such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 4,4'-azobis(4-cyanopentanoic acid), etc.; peroxide type initiators such as lauroyl peroxide, benzoyl peroxide, isobutyryl [TN: phonetic spelling] peroxide, pivaloyl tert-butyl peroxide [TN: literal translation], di-tert-butyl peroxide, etc.; redox initiators such as Fe^{2+}/hydrogen peroxide, hydrogen peroxide/ ascorbic acid, benzoyl peroxide/ dimethylaniline, etc. One kind of these or a mixture of two or more kinds can be used. Since it is more preferable to perform the polymerization at a low temperature, of these initiators, 2,2'-azobis(\4-methoxy-2,4-dimethylvaleronitrile), isobutyryl [TN: phonetic spelling] peroxide, pivaloyl tert-butyl peroxide, di-tert-butyl peroxide, and the redox initiators are more preferable.

In the method of the invention, utilizing the substitution reaction, the halogen atoms at the ends of the halogen telecheric polymer having hydrogen at the ends are converted into the hydroxyl groups. The type of substitution reaction is not specifically limited but the following four methods are effective from the aspects of reaction efficiency and difficulty in breaking of the main chain and side chains of the telecheric polymer:

1) Hydrolysis reaction;
2) substitution reaction with diol compounds;
3) substitution reaction with amine compounds having the hydroxyl group; and
4) substitution reaction with carboxylate compounds having the hydroxyl group.

Each substitution reaction is described in detail below.
The basic catalysts (d) used in the hydrolysis of the halogen atoms at the ends of the telecheric polymer having halogen at the ends may be standard basic compounds used for a hydrolysis of standard organic halides, but preferable are compounds containing an alkali metal such as sodium hydroxide, potassium hydroxide, sodium hydrogencarbonate, potassium hydrogencarbonate, sodium carbonate, potassium carbonate, etc. One kind of these or a mixture of two or more kinds of these may be used.

Regarding the mole ratio between the basic catalyst (d) and the halogen atoms at the ends of the telecheric polymer having halogen at the ends in the hydrolysis of the halogen atoms at the ends of the telecheric polymer having halogen at the ends, so long as the basic catalyst (d) is equal or greater in moles to the halogen atoms at the ends of the telecheric polymer having halogen at the ends. When the basic catalyst (d) is too little in relation to the halogen atoms at the ends of the telecheric polymer having halogen at the ends, the hydrolysis does not proceed quantitatively. When the basic catalyst (d) is too much in relation to the halogen atoms at the ends of the telecheric polymer having halogen at the ends, there is a concern that even the side chains of the polymer may be hydrolyzed in addition to the halogen atoms at the ends of the telecheric polymer having halogen at the ends. Specifically, a preferable amount of the addition of the the basic catalyst (d) in relation to the halogen atoms at the ends of the telecheric polymer having halogen at the ends is 1~10 times mole, and 3~5 times mole is more preferable.

There is no specific limitation on the solvents used for the hydrolysis of the halogen atoms at the ends of the telecheric polymer having halogen at the ends. Preferable are solvents which allow the telecheric polymer having halogen at the ends, the basic catalyst (d) and water to be near uniform during the reaction. Specifically preferable

are those solvents having high polarity such as acetone, tetrahydrofuran, dioxane, etc. However, it is not preferable to use alcohols because there is a concern that they compete for a substitution reaction, causing a formation of ether bonds and a reduction in the number of functional groups at the ends. Additives such as inter-phase transfer catalysts during the hydrolysis reaction may be freely used.

Any temperature for the hydrolysis of the halogen atoms at the ends of the telecheric polymer having the halogen at the ends can be chosen, but a preferable temperature is 20°C~100°C and more preferable is 20°C~60°C.

Examples of the diol compounds (f), represented by Formula (II)

$$HOR^2OH \qquad (II)$$

(in the formula, R^2 is a bivalent hydrocarbon group of C_1~$C_{[TN: illegible, could be "13"]}$ which may have a substitution group), and/or Formula (III)

$$HO-(R^2-O)_n-H \qquad (III)$$

(in the formula, R^2 is a bivalent hydrocarbon group of C_1~$C_{[TN: illegible, could be "13"]}$ and n is a whole number of 1~1000), which are used for the substitution reaction with halogen atoms at the ends of the telecheric polymer having the halogen at the ends are: ethylene glycol; 1,3-propanediol; 1,2-propanediol; 1,4-butanediol; 1,3-butanediol; 1,6-hexanediol; 1,8-octanediol; 1,10-decanediol; 1,12-dodecanediol; 1,18-octadecanediol; bisphenol; bisphenol hydrogenated compounds; polyethylene glycols such as diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol; polypropylene glycol; polytetramethylene glycol; etc. One kind of these or a mixture of two or more kinds of these can be used.

As the basic catalysts (e) used for the substitution reaction of the halogen atoms at the ends of the telecheric polymer having halogen at the ends and the diol compound, any basic compound can be used so long as it is used for the substitution reaction between ordinary organic halides and alcohols. But preferable are the compounds containing an alkali metal such as sodium hydroxide, potassium hydroxide, sodium hydrogencarbonate, potassium hydrogencarbonate, sodium carbonate, potassium carbonate, etc. One kind of these or a mixture of two or more kinds of these may be

used.

Regarding the mole ratio between the halogen atoms at the ends of the telecheric polymer having halogen at the ends and the diol compound (f) during the substitution reaction, it is fine so long as the diol compound (f) is equal mole to or greater in relation to the halogen atoms at the ends of the polymer having halogen at the ends. However, in order to avoid the polymer attaining a high molecular weight which is formed from a further substitution reaction between the hydroxyl groups at the end of the polymer, which had been formed by the substitution reaction, and the halogen atoms at the ends of the polymer, it is desirable that an excess of the diol compound (f) is present in relation to the halogen atoms at the ends of the polymer. Specifically, a preferable amount of the the diol compound (f) to be added in relation to the halogen atoms at the ends of the polymer is 3 times mole or greater, and more preferable is 10 times mole or greater.

There is no specific limitation for the solvent used for the substitution reaction of the halogen atoms at the ends of the telecheric polymer having halogen at the ends and the diol compound (f). However, preferable is a solvent which allows the telecheric polymer having halogen at the ends, the basic catalyst (d) and the diol compound (f) to be near uniform during the reaction. Specifically, preferable is a solvent having a high polarity such as acetone, tetrahydrofuran, dioxane, etc. However, it is not preferable to use alcohols because there is a concern that they compete for the substitution reaction, causing a formation of ether bonds and reduction in the number of the functional groups at the ends. Additives such as inter-phase transfer catalysts during the substitution reaction may be freely used.

Any temperature can be chosen for the substitution reaction of the halogen atoms at the ends of the telecheric polymer having halogen at the ends and the diol compound (f), but a preferable temperature is 20°C~100°C and 20°C~60°C is more preferable.

Examples of the amine compounds containing the hydroxyl group (g) , represented by the Formula (IV),

$$R^4NHR^5OH \qquad (IV)$$

(in the formula, R^4 is a hydrogen or an alkyl group of C_1~C [TN: illegible] and R^5 is a bivalent hydrocarbon group of C_1~C [TN: illegibl]), used for the substitution reaction with the halogen atoms at the ends of the telecheric polymer having halogen at the ends are: ethanolamine; N-methylethanolamine; N-ethylethanolamine;N-butylethanolamine; 3-hydroxypropylamine; N-methyl-3-hydroxypropylamine; 4-hydroxybutylamine; N-methyl-4-hydroxybutylamine; 6-hydroxyhexylamine; N-methyl-6-hydroxyhexylamine; 8-hydroxyoctylamin; N-methyl-8-hydroxyoctylamine; 12-hydroxydodecylamine; N-methyl-12-hydroxydodecylamine; 18-hydroxyoctadecylamine; N-methyl-18-hydroxyoctadecylamine, etc. One kind of these or a mixture of two or more kinds can be used.

The amine compound containing the hydroxyl group (g) may be a primary or secondary amine compound. However, in order to avoid the polymer attaining a higher molecular weight which is formed from a further substitution reaction between the amine group at the ends of the polymer, which had been formed during the substitution reaction, and the halogen atoms at the ends of the polymer, it is preferable that the amine compound containing the hydroxy group (g) be a secondary amine compound.

Regarding the mole ratio between the halogen atoms at the ends of the telecheric polymer having halogen at the ends and the amine compound containing the hydroxyl group (g) during the substitution reaction, it is fine so long as the amine compound containing a hydroxyl group (g) is equal or greater in moles to the halogen atoms at the ends of the polymer. However, in order avoid the polymer attaining a high molecular weight which is formed from a further substitution reaction between the hydroxyl group at the end of the polymer, which had been formed by the substitution reaction, and the halogen atoms at the ends of the polymer, it is preferable that an excess of the amine compound containing the hydroxy group (g) is present in relation to the halogen atoms at the ends of the polymer. Specifically, a preferable amount of the amine compound containing a hydroxyl group (g) to be added is 3 times mole or greater in relation to the halogen atoms at the ends of the polymer, and 10 times mole or greater is more preferable.

In addition to these, in the substitution reaction between the halogen atoms at the ends of the telecheric polymer having halogen at the ends and the amine compound containing the hydroxyl group (g), solvents, catalysts and additives such as inter-phase transfer catalysts may be freely used.

Any reaction temperature can be chosen for the substitution reaction of the halogen atoms at the ends of the telecheric polymer having halogen at the ends and the amine compound containing the hydroxyl group (g), but a preferable temperature is 20°C~100°C and more preferable is 20°C~60°C.

Examples of the carboxylate compounds containing the hydroxyl group (h), represented by Formula (V),

$$HOR^6COOM \qquad (V)$$

(in the formula, R^6 is a bivalent hydrocarbon group of C_1~C [TN: illegible] and M is an alkali metal), used for the substitution reaction with the halogen atoms at the ends of the telecheric polymer having halogen at the ends, are alkali metals of sodium and potassium such as hydroxyacetic acid, 2-hydroxypropionic acid, 3-hydroxypropionic acid, 2-hydroxy-2-methylpropionic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 2-hydroxyisovaleric acid, 2-hydroxyoctanoic acid, 3-hydroxyoctanoic acid, 2-hydroxy-decanoic acid, 3-hydroxydecanoic acid, 2-hydroxyundecanoic acid, 3-hydroxyundecanoic acid, 2-hydroxydodecanoic acid, 3-hydroxydodecanoic acid, 2-hydroxytridecanoic acid, 3-hydroxytridecanoic acid, 2-hydroxytetradecanoic acid, 3-hydroxytetradecanoic acid, 2-hydroxypentadecanoic acid, 3-hydroxypenta-decanoic acid, 2-hydroxyhexadecanoic acid, 3-hydroxyhexadecanoic acid, 12-hydroxystearic acid, 12-hydroxyoleic acid, etc. One kind of these or a mixture of two or more kinds can be used.

Regarding the mole ratio between the halogen atoms at the ends of the telecheric polymer having halogen at the ends and the carboxylate compound containing the hydroxyl group (h) during the substitution reaction, it is fine so long as the carboxylate compounds containing the hydroxyl group (h) is equal or greater in moles to the halogen atoms at the ends of the telecheric polymer having halogen at the ends.

However, preferable is 3 times mole or greater and more preferable is 5 times mole or greater.

There is no specific limitation for the solvent used for the substitution reaction of the halogen atoms at the ends of the telecheric polymer having halogen at the ends and the carboxylate compound containing the hydroxyl group (h). However, preferable is a solvent which allows the telecheric polymer having halogen at the ends and the carboxylate compounds containing the hydroxyl group (h) to be near uniform during the reaction. Specifically, preferable is a solvent having a high polarity such as acetone, tetrahydrofuran, dioxane, etc. and a mixture solvent of such highly polar solvent and water. However, it is not preferable to use alcohols because there is a concern that they compete for the substitution reaction, causing a formation of ether bonds and a reduction in the number of the functional groups at the ends. Catalysts and additives such as inter-phase transfer catalysts during the substitution reaction may be freely used.

Any reaction temperature can be chosen for the substitution reaction of the halogen atoms at the ends of the telecheric polymer having halogen at the ends and the carboxylate compounds containing the hydroxyl group (h), but a preferable temperature is 20°C~100°C and more preferable is 20°C~60°C.

The number of the functional groups at the ends of the telecheric polymer is ideally 2 in one molecule, but even if the functional group is less than 2.0, the industrial efficacy is not lost. If the average hydroxyl functional group at the ends is 1.8 or greater in one molecule, physical properties almost equal to the ideal telecheric polymer can be exhibited. Also, if the functional group is 1.5 or greater, [the telecheric polymer] can be usefully utilized in many industrial fields. Furthermore, If it is 1.0 or greater, to a certain degree it can exhibit the characteristics as a telecheric polymer, so it has industrial values.

Utilizing the reactivity of the hydroxyl group at the ends, the telecheric polymers having hydroxyl groups at the ends of the invention can be used in various applications such as a raw material for polyurethane resin, polyester resin, coating materials, adhesives,

sealing materials, etc. In addition, by reacting with (meth)acrylic acid (chloride) or 2-isocyanate ethyl methacrylate, etc., it [the telecheric polymers having the hydroxyl groups at the ends of the invention] can be easily modified to be a telecheric polymer having a polymeric unsaturated group at the ends as an effective cross-linking agent. Hence, the scope of the application is quite broad.

(Examples)

The following describe examples of the invention, but they are described only for illustrative purposes, so they are not intended to limit the scope of the invention. Below "parts and %" mean "parts by weight and % by weight."

(Reference Example 1)

In a flask equipped with 2 drip-funnels, a stirrer, a tube to introduce nitrogen, a thermometer and a reflux cooler, 500 parts of diiodomethane was placed and heated to 43°C while gradually blowing in nitrogen gas. To this, in 7 hours, there was dripped a mixture, composed of 2.9 parts of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, made by Wako Junyaku, hereafter referred to as "V-70") and 200 parts of dioxane, and 246 parts of butyl acrylate. During the drip, the temperature was maintained at 41~45°C and after the completion of the drip, stirring was continued at the same temperature for 2 hours to complete the polymerization. This produced a solution of a polymer [1]. The conversion at this time was 100%, calculated from the [TN: illegible, could be "concentration"] of the solid. Next, a solution of the polymer [1] was reduced to 5mmHg and heated to 45~50°C so as to remove the residual dioxane and diiodomethane, and further it was re-precipitated with ethanol/water, dried at 45°C under reduced pressure and the polymer [1] obtained was purified. The characteristics of the polymer [1] after the purification had a number average molecular weight of (Mn) of 5100 ((measured with a vapor pressure molecular weight measurement device (VPO)), an iodine content of 4.9% by the element analysis and the number of the iodine functional groups at the ends [Fn(I)] was 2.0.

(Reference Examples 2~6)

Polymers [2]~ [6] were obtained in the same manner as in the Reference Example 1 except that the type and the amounts of polymeric monomers, chain transfer agents

(halides) and polymerization initiators in the Reference Example 1 were used as shown in Table 1. The characteristics of the polymers [2]~[6] are shown in Table 2.

(Exampl 1)

In a flask equipped with a reflux cooler, 51 parts of the polymer [1], 200 parts of tetrahydrofuran and 6.9 parts of 35% sodium hydroxide aqueous solution were placed and allowed to react at 60°C for 6 hours while being stirred with a magnetic stirrer. After the reaction, the polymer was extracted with toluene and it was washed once with 1% sulfuric acid aqueous solution, and after that it was washed three times with ion exchange water, and finally dried at 60°C under the reduced pressure to obtain a polymer [1'].

The characteristics of the polymer [1'] were: a number average molecular weight of (Mn) of 5100 ((measured with a vapor pressure molecular weight measurement device (VPO)), an iodine content of 0.0% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 2.0. From the measurement of the acid value, it was verified that the hydrolysis of the side chains of the polymer hardly took place.

(Examples 2~4)

Polymers [2']~ [4'] were obtained in the same operation as in Example 1 except that the type and the amount of the telecheric polymers having the halogen at the ends, the type and the amount of the basic catalysts and the reaction temperatures used for the hydrolysis in Example 1 were used as shown in Table 3. The characteristics of the polymers [2']~[4'] are shown in Table 4.

(Example 5)

In a flask equipped with a reflux cooler, 51 parts of the polymer [1], 3.7 parts of ethylene glycol, 200 parts of tetrahydrofuran and 3.4 parts of 35% sodium hydroxide aqueous solution were placed and allowed to react at 25°C for 6 hours while being stirred with a magnetic stirrer. After the reaction, the polymer was extracted with toluene and it was washed once with 1% sulfuric acid aqueous solution, and after that it was washed three times with ion exchange water, and finally dried at 60°C under the

reduced pressure to obtain a polymer [5'].

The characteristics of the polymer [5'] were: a number average molecular weight of (Mn) of 5100 ((measured with a vapor pressure molecular weight measurement device (VPO)), an iodine content of 0.0% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 1.9. From the measurement of the acid value, it was verified that the hydrolysis of the side chains of the polymer hardly took place.

(Examples 6~7)

Polymers [6'] and [7'] were obtained in the same operation as in Example 5 except that the type and the amount of the telecheric polymers having the halogen at the ends, the type and amount of the diol compounds, the type and the amount of the basic catalysts and the reaction temperatures used for the substitution reaction in Example 5 were used as shown in Table 5. The characteristics of the polymers [6'] and [7'] are shown in Table 6.

(Example 8)

In a flask equipped with a reflux cooler, 51 parts of the polymer [1], 4.5 parts of N-methylethanolamine, and 200 parts of tetrahydrofuran were placed and allowed to react at 60°C for 6 hours while being stirred with a magnetic stirrer. After the reaction, excess N-methylethanolamine and tetrahydrofuran were removed by evaporation and then it was re-precipitated three times with acetone/water and finally dried at 60°C under the reduced pressure to obtain a polymer [8'].

The characteristics of the polymer [8'] were: a number average molecular weight of (Mn) of 5200 ((measured with a vapor pressure molecular weight measurement device (VPO)), an iodine content of 0.0% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 1.9. From the measurement of the acid value, it was verified that the hydrolysis of the side chains of the polymer hardly took place.

(Examples 9~10)

Polymers [9'] and [10'] were obtained in the same operation as in Example 8 except that the type and the amount of the telecheric polymers having the halogen at the ends, the type and amount of the amine compounds containing the hydroxyl group, and the reaction temperatures used in the substitution reaction in Example 8 were used as shown in Table 7. The characteristics of the polymers [9'] and [10'] are shown in Table 8.

(Example 11)

In a flask equipped with a reflux cooler, 51 parts of the polymer [1], 200 parts of tetrahydrofuran, 9.8 parts of sodium hydroxyacetate, 50 parts of ion exchange water and 1.5 parts of tetra-n-butylammonium bromide were placed and allowed to react at 60°C for 12 hours while being stirred with a magnetic stirrer. After the reaction, the polymer was extracted with toluene and was washed three times with ion exchange water, and finally dried at 60°C under reduced pressure to obtain a polymer [11']. The characteristics of the polymer [11'] were: a number average molecular weight of (Mn) of 5300 ((measured with a vapor pressure molecular weight measurement device (VPO)), an iodine content of 0.3% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 1.8. From the measurement of the acid value, it was verified that the hydrolysis of the side chains of the polymer hardly took place.

(Examples 12~13)

Polymers [12'] and [13'] were obtained in the same operation as in Example 11 except that the type and the amount of the telecheric polymers having the halogen at the ends, the type and amount of the carboxylate compounds containing the hydroxyl group, and the reaction temperatures used in the substitution reaction in Example 11 were used as shown in Table 9. The characteristics of the polymers [12'] and [13'] are shown in Table 10.

(Example 14~15)

Polymers [14'] and [15'] were obtained in the same operation as in Example 1 except that the amount of the 35% sodium hydroxide aqueous solution in Example 1 was

used as shown in Table 11. The characteristics of the polymers [14'] and [15'] are shown in Table 11.

(Exampl 16)

A polymers [16'] was obtained in the same operation as in Example 5 except that the amount of addition of ethylene glycol in Example 5 was changed to 1.4 parts. The characteristics of the polymers [16'] were: a number average molecular weight of (Mn) of 7400 ((measured with a vapor pressure molecular weight measurement device (VPO)), an iodine content of 0.9% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 1.6. From the measurement of the acid value, it was verified that the hydrolysis of the side chains of the polymer hardly took place.

(Example 17)

A polymers [17'] was obtained in the same operation as in Example 8 except that the amount of addition of N-methylethanolamine in Example 8 was changed to 1.8 parts. The characteristics of the polymers [17'] were: a number average molecular weight of (Mn) of 6200 ((measured with a vapor pressure molecular weight measurement device (VPO)), an iodine content of 1.2% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 1.5. From the measurement of the acid value, it was verified that the hydrolysis of the side chains of the polymer hardly took place.

(Example 18)

A polymers [18'] was obtained in the same operation as in Example 11 except that the amount of addition of sodium hydroxyacetate in Example 11 was changed to 3.9 parts in Example 11. The characteristics of the polymers [18'] were: a number average molecular weight of (Mn) of 5900 ((measured with a vapor pressure molecular weight measurement device (VPO)), an iodine content of 1.7% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 1.3.

(Comparison Reference Example 1)

A comparison reference example polymer [1] was obtained in the same operation as

in Reference Example 1 except for: using 24 parts of butyl acrylate, 15900 parts of dichloromethane (mole ratio between polymeric monomer/dichloromethane: 0.01) instead of 500 parts of diiodomathane, 144 parts of V-70 (mole ratio between dichloromathane/V-70: 400) and 300 parts of dioxane in Reference Example 1. The characteristics of comparison reference example polymer [1] are as shown in Table 12.

(Comparison Reference Example 2)

A comparison reference example polymer [2] was obtained in the same operation as in Reference Example 1 except for: using 58400 parts of 1,12-dibromododecane (mole ratio between polymeric monomer/1,12-dibromododecane: 0.01) instead of 500 parts of diiodomathane, 144 parts of V-70 (mole ratio between 1,12-dibromododecane /V-70: 400) and 300 parts of dioxane in Reference Example 1. The characteristics of the comparison reference example polymer [2] were as shown in Table 12.

(Comparison Reference Example 3)

A comparison reference example polymer [3] was obtained in the same operation as in Reference Example 1 except for: using 34.3 parts of diiodomethane (mole ratio between polymeric monomer/diiodomethane: 15) in Reference Example 1 and adding 500 parts of dioxane in a vessel at the initial stage. The characteristics of the comparison reference example polymer [1] are as shown in Table 12.

(Comparison Reference Example 4)

A comparison reference example polymer [4] was obtained in the same operation as in Reference Example 1 except for: using 62000 parts of diiodomethane (mole ratio between polymeric monomer/diiodomethane: 0.0083) and 179 parts of V-70 (mole ratio between diiodomethane/V-70: 400) in Reference Example 1. The characteristics of the comparison reference example polymer [4] are as shown in Table 12.

(Comparison Example 1)

A comparison polymer [1'] was obtained in the same operation as in Example 1 except for using: 1130 parts of the comparison reference polymer [1], instead of 51 parts of the polymer [1], and 2000 parts of tetrahydrofuran in the Example 1 . The

characteristics of the comparison polymer [1'] were: a number average molecular weight of (Mn) of 11800 (measured with GPC using the analytical curve according to the standard polystyrene), an iodine content of 0.00% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 0.5.

(Comparison Example 2)

A comparison polymer [2'] was obtained in the same operation as in Example 5 except for using: 1020 parts of the comparison reference polymer [2], instead of 51 parts of the polymer [1], and 2000 parts of tetrahydrofuran in the Example 1. The characteristics of the comparison polymer [2'] were: a number average molecular weight of (Mn) of 110000 (measured with GPC using the analytical curve according to the standard polystyrene), an iodine content of 0.00% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 0.5.

(Comparison Example 3)

A comparison polymer [3'] was obtained in the same operation as in Example 8 except for using: 970 parts of the comparison reference polymer [3], instead of 51 parts of the polymer [1], and 1000 parts of tetrahydrofuran as in the Example 8. The characteristics of the comparison polymer [3'] were: a number average molecular weight of (Mn) of 100000 (measured with GPC using the analytical curve according to the standard polystyrene), an iodine content of 0.00% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 0.6.

(Comparison Example 4)

A comparison polymer [4'] was obtained in the same operation as in Example 11 except for using: 970 parts of the comparison reference polymer [3], instead of 51 parts of the polymer [1], and 1000 parts of tetrahydrofuran, and 15 parts of tetra-n-butylammonium bromide as in the Example 11. The characteristics of the comparison polymer [4'] were: a number average molecular weight of (Mn) of 103000 (measured with GPC using the analytical curve according to the standard polystyrene), an iodine content of 0.02% by the element analysis and the number of the OH functional groups at the ends [Fn(OH)] was 0.5.

(Eff cts of th Inv ntion)

The present invention is a process to manufacture easily and inexpensively a telecheric polymer having the hydroxyl group at the ends: which itself is useful as a raw material for various resins such as polyurethane resin, polyester resin, etc., coating materials, adhesives, sealing materials, etc.; which can be used as a precursor of a telecheric polymer having the polymeric unsaturated ends such as acryloyl group and methacryloyl group for cross-linking; of which the scope of application is quite broad; and which is quite useful industrially.

The use of the invention permits, using industrially used radical polymerization, an easy and inexpensive manufacture of a telecheric polymer having the hydroxyl group at the ends from a quite broad range of polymeric monomers including polar polymeric monomers such as acrylic esters and methacrylic esters, which in the past was difficult.

Table 1

Reference Example	Polymeric monomer	parts by wt.	Chain transfer agent (halogen compound)	parts by wt.	Polymerization initiator	parts by wt.
2	Styrene	187	Dibromomethane	313	Pivaloyl tert-butyl-peroxide [TN: literal translation]	3.1
3	2-ethylhexyl acrylate Styrene	241 59	1,2-diiodoethane	250	"	"
4	Methyl methacrylate Styrene Acrylonitrile	94 99 10	Dibromomethane	650	Pivaloyl tert-butyl-peroxide	3.3
5	Methyl methacrylate Phenyl maleimide	95 151	1,2-diiodoethane	500	"	"

Table 2

Polymer	Conversion (%)	Number average molecular weight (measured by VPO)	Halogen Content (wt%)	Number of halogen functional groups at nds (atom/polymer 1 molecule)
[2]	98	61000*	0.24	1.8
[3]	98	9900	2.4	1.9
[4]	97	32000*	0.48	1.9
[5]	98	5600	4.4	1.9

* Measured with GPC using the analytical curve of the standard polystyrene.

Table 3

Polymer	Telecheric polymer w/ halogen at ends	(parts by wt.)	Basic catalyst	parts by wt.	Reaction temp. (°C)
[2']	Polymer [2]	61	35% potassium hydroxide aqueous solution	1.6	25
[3']	Polymer [3]	99	10% sodium hydrocarbonate aqueous solution	84	60
[4']	Polymer [4]	320	35% sodium hydroxide aqueous solution	6.9	40
[5']	Polymer [5]	56	10% potassium carbonate aqueous solution	83	60

Table 4

Polymer	Number average molecular weight (measured by VPO)	Halogen Content (wt%)	Number of hydroxyl functional groups at ends (mole/polymer 1 mole)**
[2']	61000*	0.0	1.8
[3']	9900	0.1	1.8
[4']	32000*	0.0	1.9
[5']	5600	0.1	1.9

* Measured with GPC using the analytical curve of the standard polystyrene

** Calculated from the concentration of the hydroxyl groups of each polymer obtained from the acetylation method (in accordance with JIS K 1557) and the number average molecular weight of each polymer obtained from VPO (GPC).

Tabl 5

Polymer	Telecheric polymer w/ halog n at ends (wt. parts)		Diol compound (wt.parts)		Basic catalyst (wt.parts)		Reaction t mp. (°C)
[6']	Polymer [2]	61	Polyethylene glycol*	12	35% sodium hydroxide aqueous solution	2.3	60
[7']	Polymer [3]	99	1, 4-butane diol	9	35% potassium hydroxide aqueous solution	9.6	25

* PEG 600 (average molecular weight: 600, hydroxyl group value: 187, made by Sanyo Kasei .

Table 6

Polymer	Number average molecular weight (measured by VPO)	Halogen Content (wt%)	Number of hydroxyl functional groups at ends (mole/polymer 1 mole)**
[6']	64000*	0.0	1.8
[7']	10000	0.0	1.9

* Measured with GPC using the analytical curve of the standard polystyrene

** Calculated from the concentration of the hydroxyl groups of each polymer obtained from the acetylation method (in accordance with JIS K 1557) and the number average molecular weight of each polymer obtained from VPO (GPC).

Table 7

Polymer	Telecheric polymer w/ halogen at ends	(parts by wt.)	Amine compound containing hydroxyl group	parts by wt.	Reaction temp. (°C)
[9']	Polymer [4]	160	Ethanol amine aqueous solution	1.6	60
[10']	Polymer [5]	56	3-hydroxypropylamine aqueous solution	30	25

Table 8

Polymer	Number average molecular weight (measured by VPO)	Halogen Content (wt%)	Number of hydroxyl functional groups at nds (mole/polymer 1 mole)**
[9']	32000*	0.0	1:9
[10']	5800	0.0	1.9

* Measured with GPC using the analytical curve of the standard polystyrene

** Calculated from the concentration of the hydroxyl groups of each polymer obtained from the acetylation (method [n accordance with JIS K 1557) and the number average molecular weight of each polymer obtained from VPO (GPC).

Table 9

Polymer	Telecheric polymer w/ halogen at ends	(parts by wt.)	Carboxylate compound containing hydroxyl l group	parts by wt.	Reaction temp. (°C)
[12']	Polymer [3]	99	potassium 2-hydroxy-butyrate	14	60
[13']	Polymer [5]	56	sodium 2-hydroxyoctanate	18	60

Table 10

Polymer	Number average molecular weight (measured by VPO)	Halogen Content (wt%)	Number of hydroxyl functional groups at ends (mole/polymer 1 mole)*
[12''']	10000*	0.2	1.7
[13']	6200	0.3	1.8

* Calculated from the concentration of the hydroxyl groups of each polymer obtained from the acetylation method (in accordance with JIS K 1557) and the number average molecular weight of each polymer obtained from VPO (GPC).

Tabl 11

Polymer	Amount of addition of 35% sodium hydroxide (parts)	Number average molecular weight (measured by VPO)	Halogen Content (wt%)	No. of hydroxyl functional groups at ends (mole/polymer 1 mole)*	Remarks
[14']	2.3	5500	1.2	1.5	
[15']	34	5100	0.0	2.0	Hydrolysis of the side chains was observed to a great extent.

* Calculated from the concentration of the hydroxy I groups of each polymer obtained from the acetylation method (in accordance with JIS K 1557) and the number average molecular weight of each polymer obtained from VPO (GPC).

Table 12

Comparison Examp. polymer	Conversion (%)	Number average molecular weight (measured by VPO)	Halogen Content (wt%)	No. of hydroxyl functional groups at ends (mole/polymer 1 mole)	Remarks
(1)	97	113000*	0.02	0.6	Use of dichloromethane as halogen compound
(2)	98	102000*	0.05	0.7	Use of 1,12-dibromo-dodecane as halogen compound
(3)	99	97000*	0.09	0.7	Mole ratio between polymeric monomer and diiodomethane: 15.
(4)	33	690	36.8	2.0	Mole ratio between polymeric monomer and diiodomethane: 0.0083.

* Measured with GPC using the analytical curve of the standard polystyrene.